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## (54) WATER-REACTIVE SOLID DEODORISING COMPOSITION

(71) We, OLIN CORPORATION, formerly known as Olin Mathieson Chemical Corporation, a corporation organised and existing under the laws of the State of Virginia, United States of America, having its offices at 275 Winchester Avenue, New Haven, Connecticut 06504, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to deodorizing compositions and to a method of using them. More particularly, it provides solid compositions containing available halogen, an effervescent couple and solid polyolefin. When these compositions are placed in water, they float. The gases formed by reaction between the water and the components of the tablet are substantially completely delivered into the air space above the water and selectively react with the odorous vapors and thus deodorize the air in the air space. The compositions of this invention finds particular utility in the treatment of air space in the bowl of water closets, in bedpans and in other and larger locations.

Various compositions of the prior art have been prepared and added to the water in water closets for the purposes of sanitizing and disinfecting the aqueous content. Such compositions contain a sanitizing agent which is dispersed in the water and acts in the water to sanitize water. Known compositions for these purposes have no discernible effect on the air space above the water which is usually malodorous and repulsive. Effervescent compositions, particularly tablets, have been proposed where the purpose of the effervescent couple is to promote rapid disintegration of the tablet in water and rapid dis-

solution of the germicidal agents in the water. The tablets of British patent 955,897 and U.S. patent 3,120,378, for example, have been found to be heavier than water and lie on the bottom of the container while they react with the water. All the sanitizing agent remains dispersed in the water and never reaches the air space above the water. The gases are effectively scrubbed by passage through the water and any chlorinous, deodorizing compounds of the gases never reach the air space above the water. They are ineffective to supply any significant amount of deodorizing material to the air space above the body of water to which they are added and they are ineffective to deodorize the air spaces. The incorporation of magnesium carbonate, suggested as a floatable component of certain available chlorine compositions in U.S. patent 3,236,726, forms an unattractive scum on the surface of the water. The purpose of this film is to keep the chloring in the water phase for stain-removing purposes and to lengthen the period of chlorination without substantial escape of the vapors to the air. Insofar as the chlorine is kept in the water, it is not delivered into the air space and is substantially ineffective in deodorizing the air space above the water.

In brief, the invention provides, subject to a disclaimer set out below, a solid deodorizing composition reactive with water to generate and deliver a halogenous deodorizing gas into the air space above a body of water into which said composition is introduced and on which said composition floats, said composition comprising an intimate mixture of the following ingredients in particulate form:

- (1) a solid source of available chlorine or of available bromine;

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- (2) a solid gas-generating source non-reactive with the solid source of available chlorine or bromine but reactive with water to generate a gas; and  
 5 (3) a solid polymer of an aliphatic olefin having 2 to 5 carbon atoms.

In contrast to the composition of the prior art which sanitize the water only, the compositions of the present invention float on or near the top of the body of water to which they are added. They are reactive with water to generate halogenous gases and to deliver them substantially completely to the air space above the body of water to which they are added. The halogenous gases quickly deodorize the air space and keep it deodorized as necessary. Compositions of the prior art which, when added to water, sink to the bottom and react to form gaseous products, deliver their gases at the bottom where they are scrubbed in ascending through the water. Any sanitizing agent therein is retained by and is active in the water but substantially no sanitizing gas is delivered to the air space above the water and they are ineffective to deodorize the air space.

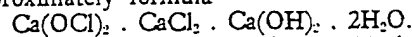
In using the compositions of this invention, a suitable portion of the composition is added to the toilet bowl preferably immediately prior to use. Reaction with the water starts immediately and continues during normal use. The composition reacts and delivers halogenous gases to the air space above the water and the halogenous gases react with odorous materials, for example, hydrogen sulfide in the air space to convert it to non-odorous products. The halogenous gases thus sweeten and deodorize the air space.

The compositions of the invention quickly produce halogenous gases when added to water and deliver the halogenous gases into the air space by the floating action of the compositions of the present invention rather than dissolving largely in water. The halogenous gases may be produced in quantities sufficient to deodorize quickly and thoroughly the offensive gases in the air space, for example, in the toilet bowl when in use. The composition of the halogenous gases is not certainly known and probably includes chlorine, chlorine monoxide and other components. The term "halogenous gases" as used herein is understood to include such gases and gases so generated even though their total composition is not certainly known.

The solid source of available chlorine (which is the preferred halogen) is suitably any of a wide variety of available chlorine compounds, including both organic and inorganic types. Suitable organic available chlorine compounds include particularly the N - chloro - compounds, for example, the chloroisocyanurates, dichloroisocyanuric acid, trichloroisocyanuric acid, sodium, potassium

and calcium dichloroisocyanurates and other dichloroisocyanuric acid salts, including heavy metal salts, double salts and mixtures thereof. Other suitable N - chloro - organics include 1,3 - dichloro - 5,5 - dimethylhydantoin, chloramine T, dichloramine T, N - chloro - succinimide, N,N' - dichlorobenzoylene urea, trichloromelamine, 1,3,4,6 - tetrachloroglycoluril and other organic available chlorine compounds.

A preferred solid source of available chlorine for the purposes of this invention is an inorganic hypochlorite, and, more particularly, alkali metal and alkaline earth hypochlorites including magnesium hypochlorite. The alkali metal hypochlorites include particularly lithium hypochlorite both anhydrous and monohydrate, and solid forms of sodium hypochlorite including partially chlorinated caustic, e.g.,  $\text{NaOCl} \cdot 3\text{NaOH}$  and chlorinated trisodium phosphate,  $\text{Na}_3\text{PO}_4 \cdot 1/3 \text{NaOCl} \cdot 11-2/3 \text{H}_2\text{O}$ . Neutral alkaline earth metal hypochlorites include calcium hypochlorite, barium hypochlorite, strontium hypochlorite and magnesium hypochlorite. Basic calcium hypochlorites are suitable, including hemibasic and dibasic having the formulas  $\text{Ca}(\text{OCl})_2 \cdot 1/2\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{OCl})_2 \cdot 2\text{Ca}(\text{OH})_2$ , respectively. Also suitable in some compositions is chlorinated lime having the approximately formula



The solid source of available chlorine is suitably any of the types described but the hypochlorites, in general, liberate available chlorine at a faster rate than the N - chloro - compounds in the environment here used. The use of twice or three times the proportion of N - chloro - compound usually compensates for the slower liberation rate and makes the N - chloro - compounds satisfactory. The N - chloro - compounds are more expensive per unit of available chlorine than many of the hypochlorites, particularly calcium hypochlorite, and these compositions are more expensive to manufacture than those based on the hypochlorites. The effectiveness of the N - chloro - compounds in the present environment is also increased by addition of acid to the compositions or to the water to which the compositions are added. Addition of acid to water requires a separate operation and also increases the cost.

Alkali metal hypochlorites, particularly lithium hypochlorite and sodium hypochlorite, are effective sources of available chlorine and, in the environment here used, liberate chlorinous gases more rapidly than the N - chloro compounds. Of the alkaline earth metal hypochlorites, magnesium, barium and strontium hypochlorites liberate their available chlorine readily, although they are more expensive than calcium hypochlorite. Basic calcium hypochlorites and chlorinated lime have low available chlorine contents compared with

high test calcium hypochlorite and require additional acid to neutralize their alkalinity.

For the above reasons, high test calcium hypochlorite is the preferred hypochlorite in the compositions of this invention. It has the advantages of lowest cost, highest available chlorine content, most rapid liberation of chlorinous gases, stability and commercial availability.

In order to provide in the compositions of this invention suitable proportions of effervescent couple and polyolefin as well as desirable but lesser amounts of lubricants, stabilizers, desiccants and other ingredients, it is advantageous to use alkali metal or alkaline earth metal hypochlorites of high available chlorine content as the source of that component. Calcium hypochlorites as commercially available containing 70 percent or more of available chlorine is especially advantageous for this additional reason.

A particularly preferred alkaline earth metal hypochlorite suitable for the purposes of the present invention is calcium hypochlorite containing 70 percent or more of available chlorine. Hypochlorite fines are useful in the present invention and are obtained as a by-product in the manufacture of granular material which is sold commercially. However, other grades of calcium hypochlorite are useful and the granular material can be reduced to fines by comminution. Preferably the calcium hypochlorite contains at least 25 percent finer than 100 mesh (U. S. Standard Screens) and none coarser than 30 mesh. Calcium hypochlorite compositions containing over 35 percent or more of available chlorine are especially suitable for use in the compositions of the present invention.

Suitable powdered calcium hypochlorite, known as HTH fines has, for example, the screen analysis shown below:

| Screen           | Weight<br>Percent |
|------------------|-------------------|
| In 50 mesh       | 0.4               |
| On 70 mesh       | 18.9              |
| On 100 mesh      | 33.4              |
| On 200 mesh      | 29.3              |
| Through 200 mesh | 18.0              |
| 50               | 100.0             |

A suitable solid gas-generating source is stable and non-reactive when mixed with the available halogen compound used in any particular composition of this invention and the solid gas-generating source is reactive with water to generate a gas. The gas acts as a carrier for the halogenous gases from the available halogen compound into the air space. Although any gas-generating source compatible with the available halogen compound is suitable, the preferred gas-generating source contains a solid carbonate and a solid acid.

In contact with water, these react instantly to generate carbon dioxide gas. Preferred carbonates are the alkali metal and alkaline earth metal carbonates and bicarbonates including sodium carbonate, sodium bicarbonate, potassium bicarbonate, lithium bicarbonate, rubidium carbonate, cesium bicarbonate, sodium potassium carbonate, calcium carbonate and magnesium carbonate.

Suitable solid acids are organic or inorganic and include solid organic carboxylic acids and solid acid salts, for example, oxalic, succinic, tartaric, citric, gluconic, malic, malonic, maleic, phthalic and p-toluene sulfonic acids and sodium acid citrate, potassium bitartrate, potassium acid phthalate, sodium acid oxalate, rubidium acid tartrate, cesium acid tartrate and lithium acid citrate. Chloroisocyanuric acids also suitably serve as the acid component. Suitable solid acid compounds also include solid inorganic acids and solid acid salts, for example, potassium dihydrogen phosphate, sodium dihydrogen phosphate, sodium dihydrogen pyrophosphate ( $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ), sulfamic acid and sodium bisulfate. Another suitable solid acid compound is ammoniated  $\text{P}_2\text{O}_5$ , an ammonium polyphosphate-coated  $\text{P}_2\text{O}_5$ , sold under the trade name "N- $\text{P}_2\text{O}_5$ ".

The preferred couple is citric acid and sodium bicarbonate.

The carbonate and the acidic compound are suitably used in a wide range of relative proportions. The acidic compound is preferably used in amounts of from 2.5 to 25 percent by weight of the total consumption, with approximately an equal weight of sodium bicarbonate when used or about half its weight when sodium carbonate is used or proportional amounts of other carbonates or bicarbonates. The total proportion of gas-generating source in the compositions of the present invention are preferably from about 5 to 50 percent by weight of the total composition.

The solid polyolefin component of the compositions of the present invention is suitably a polymer of an aliphatic olefin having 2 to 5 carbon atoms. Suitable solid co-polymers having a major proportion of the olefin (or diolefin) units but also containing a minor proportion of vinyl monomer units, may be used. Such solid polyolefins are usually waxy or rubbery but all are of lower density and substantially inert to available chlorine compounds. Particular examples include polyethylene, polypropylene and polybutadiene. Commercially available polyethylene or polypropylene are preferred. Either the commercially available finely powdered polyethylene or the microfine polyethylene consisting of spherical particles of under 20 micron size are especially suitable. Polypropylene, commercially available as powder or fiber, is suitable. The polyolefin content of the compositions of this invention is sufficient to insure

that the compositions float while reacting with water. Although polyolefine content is preferably from 10 to 50 percent by weight of the total composition, less than 10 percent of especially low-density polyolefine is sufficient in combination with other light weight components, to produce compositions which float on water. More than 50 percent polyolefin is suitable when small proportions of available halogen compounds, effervescent couple and other ingredients in lesser amounts are present in the composition. For these reasons, it is desirable, in some compositions of the invention, to use proportions outside the limits of the preferred range.

The solid polyolefins used in the compositions of this invention have outstanding and unpredictable advantages over any other materials for the purpose. The solid polyolefins have low density and are effective in floating the compositions on water. The solid polyolefins are odorless, inert and stable to available halogen compounds. They are especially advantageous in being resilient and contributing lubricating properties to compositions of the invention when produced in tablet form. In other compositions in non-tablet form, the solid polyolefins contribute advantageous non-dusting properties.

The compositions of this invention contain the three principal components and the minor components, when present, in a wide range of relative proportions and all of these compositions are useful and effective in varying environments. For many purposes, the compositions of this invention contain advantageously from 1 to 40 percent by weight available of hydrogen source, from 5 to 50 percent by weight of the solid gas-generating source and from about 10 to 50 percent by weight of polyolefin. The proportion of available halogen source varies according to the available halogen content of the source. For example, 7 percent of available chlorine in the final composition requires the incorporation therein of 10 percent of high test calcium hypochlorite containing 70 percent available chlorine. The preferred proportion of available chlorine in the compositions of this invention, when using calcium hypochlorite as the source of available chlorine, is 1 to 10 percent by weight of available chlorine.

In addition to the three major components of the composition of the present invention, namely, (1) the available halogen source, (2) the solid gas-generating source and (3) the polyolefin, it is usually desirable to include minor ingredients in lesser amounts. These minor ingredients include diluent salts, desiccants, binders, fillers, lubricants, disintegrants, pigments and perfumes.

Suitable diluent salts, when used, are water-soluble inorganic salts which are non-reactive with calcium hypochlorite and which do not adversely affect is stability. Sodium chloride

and sodium nitrate are especially useful as diluent salts which are stable to and otherwise compatible with calcium hypochlorite and other available chlorine compounds. Both of these salts are advantageously readily soluble in water and facilitate rapid dissolution of the effervescent compositions of the present invention in tablet form when they are added to a body of water. Other suitable diluent salts include, for example, sodium chlorate, potassium chlorate, potassium chloride, potassium nitrate and lithium chloride. The inclusion of a chloride, for example, sodium chloride or potassium chloride, is preferred since chlorides seem to improve the deodorizing ability of the evolved gases. The proportion of diluent salts, when included, is suitably up to about 15 percent. The diluent salts, when used, need not meet particular fineness specifications as this is not critical. However, the added diluent salt should preferably pass 30 mesh but may be all retained no 100 mesh. The so-called "butterflake" salt having an apparent density of 0.7 to 0.9 is suitable. Microfine salt is an advantageous form of salt in many compositions of this invention.

The inclusion of a solid, substantially neutral desiccant in the composition is desirable to prevent premature decomposition of the composition by atmospheric moisture. However, where individual portions are packaged in impervious plastic envelopes or sealed between sheets of plastic, the amount of desiccant is suitably reduced and can be eliminated. When used, the desiccant is suitably from 15 to 30 percent by weight of the composition. Suitable desiccants include Drierite (anhydrous calcium sulfate), alumina and silica gel.

Suitable lubricants include stearic acid and the stearates of sodium, lithium, magnesium, zinc and aluminium and conventional lubricants especially appropriate for tableting the compositions of this invention. Carboxymethyl cellulose, hydroxyethyl cellulose and CMHEC 37M, a mixed carboxymethyl - hydroxyethyl cellulose are other suitable lubricants CMHEC 37M also acts as a binder but other suitable binders are also useful.

Suitable binders include, for example CMHEC 37 M, hydroxypropylcellulose, hydroxyethylcellulose, methyl vinyl ether-maleic anhydride co-polymers, polyethylene glycol polymers, chlorinated polypropylene, polyvinylpyrrolidone, acacia gum and agar.

A particularly desirable filler, conferring good tableting properties to the composition is "Cab-O-Sil", a silica which is finely-divided to submicron size particles.

Suitable pigments include Monarch (Trade Mark) Blue Toner, a phthalocyanine blue, as well as the inorganic pigments, for example, chromium oxide ( $\text{Cr}_2\text{O}_3$ ) and cosmetic green.

Inclusion of a perfume is usually desirable.

Pine type or floral odors are suitable. Particularly suitable is a banana (ester-type) odor. Advantageously, the perfume is adsorbed in a suitable salt or adsorbant clay, for example, Microcel E, a finely divided hydrous calcium silicate.

The compositions of this invention are produced in any suitable form, including powders, granular mixtures, tablets and any other desired form. Tablets are preferred for convenience in handling, packaging and use in appropriate dosages. To provide satisfactory tableting conditions, for example, freedom from sticking and pitting and to provide tablets having adequate strength and stability, it is advantageous to include in the compositions of this invention binders, fillers and lubricants.

In tableting the compositions of this invention, it is advantageous for the ingredients to have a range of particle size, suitably from 30 mesh through 200 mesh. All of one ingredient can have a narrow range of particle sizes provided other ingredients provide the desirable over-all distribution of particle sizes. HTH fines or microfine polyethylene conveniently supply the finer ingredients. The diluent salt and citric acid need not be so fine but, for satisfactory tableting, all should pass 30 mesh and at least 10 percent should pass 100 mesh.

Tableting is accomplished in any of the commercially available machines, suitably at pressures of about 5000 to 80,000 psi or higher. Lower pressures generally result in fragile tablets which do not adequately withstand ordinary handling and shipping. The higher pressures are suitable with larger proportions of polyolefin but generally pressures in the middle of the recited range, from 10,000 to 50,000, are preferred. Too little polyolefin may result in non-floating tablets but satisfactory floating tablets are produced when additional polyolefin is blended in or when tableting pressures are reduced, or both.

Tablets are suitably marketed in bulk, in glass bottles, plastic tubes or any other suitable containers. The tablets are also suitably enclosed between sheets of plastic or aluminum foil, in plastic bags, for example, of polyethylene, in bags formed from laid fibers or in any other suitable packages. The tableted compositions of this invention are safe, stable and strong.

Compositions of this invention in non-tablet form, for example, in powdered or granular form are conveniently dispensed in any suitable containers, for example, glass bottles, polyethylene bottles or polyethylene-lined metal containers, advantageously fitted with dispensing and/or measuring features for proper dosage. Additionally powders are arranged in pockets between sheets of plastic which is water-permeable or water-impermeable or between sheets of aluminum foil.

These are readily torn open and the contents placed in use. These compositions are conveniently packaged and carried in pocket or purse for handy use.

In the following examples, all parts are parts by weight.

#### EXAMPLE I

A base formula was prepared by blending thoroughly the following ingredients in the proportions indicated:

| Ingredient  | Parts by weight |    |
|---|-----------------|----|
| NaHCO <sub>3</sub> , Powder                       | 628.0           |    |
| Microcel E  | 72.5            |    |
| NaCl, microsize                                   | 198.1           | 80 |
| Polyethylene Powder                               | 1449.2          |    |
| Cab-o-Sil M-5                                     | 169.1           |    |
| Carboxymethylhydroxyethyl-cellulose 37M. -70 Mesh | 217.4           |    |
| Sodium Stearate                                   | 217.4           | 85 |
| Lithium Stearate                                  | 48.3            |    |
| Total   | 3000.0          |    |

A composition of the invention was prepared by thoroughly blending a portion of the above base formula with addition ingredients in the proportions indicated:

| Ingredient                                    | Parts by weight |     |
|---|-----------------|-----|
| Base formula                                  | 62.10           |     |
| Citric acid powder                            | 8.15            | 95  |
| Citric acid, fine granular                    | 8.15            |     |
| Drierite, -40 mesh                            | 7.60            |     |
| LiOCl (2.3% H <sub>2</sub> O, 26.27% Av. Cl.) | 14.00           |     |
| Total   | 100.00          | 100 |

Tablets of the invention were formed from the above blend in a hand press at 6000 psi. The tablets were 9/16 inch in diameter and weighed 0.75 grams each. The thickness was about 3/8 inch. (For comparative purposes in these examples, the thickness varied depending principally on the nature of the ingredients and the tableting pressure while the diameter and weight of the tablets was kept constant).

A single tablet floated on 1500 ml. of water at 15°C. and disintegrated rapidly delivering to the air space 3 ppm of available chlorine in 30 seconds and 15 ppm in 10 minutes.

#### EXAMPLE II

A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|   | Ingredients  | Parts by weight | Ingredients         | Parts by weight |    |
|---|--|-----------------|---------------------|-----------------|----|
|   | Base formula of Example I                                    | 6.21            | Base formula        | 62.1            |    |
|   | Citric acid, powder  | 3.09            | Citric acid, powder | 23.9            |    |
| 5 | Ca(OCl) <sub>2</sub> · 2Ca(OH) <sub>2</sub><br>(50% av. Cl.) | 0.70            | "ACL-66"            | 14.0            | 55 |
|   | Total  | 10.00           | Total               | 100.0           |    |

10 Tableted as described in Example I and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 8 ppm of available chlorine in 30 seconds and 23 ppm in 10 minutes.

#### EXAMPLE III

15 A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|    | Ingredients                         | Parts by weight |
|----|-------------------------------------|-----------------|
|    | Base formula                        | 62.10           |
|    | Citric acid, powder                 | 11.95           |
|    | Citric acid, fine granular          | 11.95           |
|    | Chlorinated lime<br>(36.3% av. Cl.) | 14.00           |
| 20 | Total                               | 100.00          |

25 Tableted as described in Example I at 4000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 7 ppm in 30 seconds and 43 ppm in 10 minutes.

#### EXAMPLE IV

A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|    | Ingredients                 | Parts by weight |
|----|-----------------------------|-----------------|
|    | Base formula                | 62.1            |
|    | Sodium dichloroisocyanurate | 10.0            |
|    | Citric acid, powder         | 27.9            |
| 35 | Total                       | 100.0           |

40 Tableted as described in Example I at 7000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 2 ppm of available chlorine in 30 seconds and 9 ppm in 10 minutes.

#### EXAMPLE V

50 A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

"ACL-66" is a commercial product identified as [(mono - trichloro)tetra(monopotassium dichloro)] penta - isocyanurate.

60 Tableted as described in Example I at 7000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 2 ppm of available chlorine in 30 seconds and 10 ppm in 10 minutes.

#### EXAMPLE VI

A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|  | Ingredients                | Parts by weight |    |
|--|----------------------------|-----------------|----|
|  | Base formula               | 62.1            |    |
|  | Dichloroisocyanuric acid   | 14.0            |    |
|  | Citric acid, fine granular | 23.9            |    |
|  | Total                      | 100.0           | 70 |

75 Tableted as described in Example I at 6000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 1 ppm of available chlorine in 30 seconds and 7 ppm in 10 minutes.

#### EXAMPLE VII

A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|  | Ingredients               | Parts by weight |    |
|--|---------------------------|-----------------|----|
|  | Base formula              | 62.1            |    |
|  | Trichloroisocyanuric acid | 14.0            |    |
|  | Citric acid, powder       | 23.9            |    |
|  | Total                     | 100.0           | 80 |

85 Tableted as described in Example I, at 8000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 3 ppm of available chlorine in 30 seconds and 17 ppm in 10 minutes.

#### EXAMPLE VIII

A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|   |   |                 |  |    |
|---|---|-----------------|--|----|
|   | Ingredients   | Parts by weight | Tabletting as described in Example I at 6000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 1 ppm of available chlorine in 30 seconds and 6 ppm in 10 minutes. | 55 |
|   | Base formula  | 62.1            |  |    |
|   | "Daxan" (Tetrachloroglycoluril)   | 14.0            |  |    |
| 5 | N—P <sub>2</sub> O <sub>5</sub> (Stabilized P <sub>2</sub> O <sub>5</sub> ) | 23.9            |  |    |
|   | Total   | 100.0           |  | 60 |

Tabletting as described in Example I at 7000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 1 ppm of available chlorine in 30 seconds and 29 ppm in 10 minutes.

#### EXAMPLE IX

A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|    |                       |                 |   |    |
|----|-----------------------|-----------------|---|----|
|    | Ingredients           | Parts by weight | Tabletting as described in Example I at 10,000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 4 ppm of available chlorine in 30 seconds and 11 ppm in 10 minutes. | 75 |
|    | Base formula          | 62.1            |   |    |
| 20 | N - chlorosuccinimide | 14.0            |   |    |
|    | Citric acid, powder   | 23.9            |   |    |
|    | Total                 | 100.0           |   | 70 |

Tabletting as described in Example I at 6000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 0.4 ppm of available chlorine in 30 seconds and 2 ppm in 10 minutes.

#### EXAMPLE X

A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|  |                      |                 |   |     |
|--|----------------------|-----------------|---|-----|
|  | Ingredients          | Parts by weight | Tabletting as described in Example I at 7000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 1 ppm of available bromine in 30 seconds and 6 ppm in 10 minutes. | 100 |
|  | Base formula         | 62.1            |   |     |
|  | N - Bromosuccinimide | 14.0            |   |     |
|  | Citric acid, powder  | 23.9            |   |     |
|  | Total                | 100.0           |   | 105 |

Tabletting as described in Example I at 6000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 1 ppm of available chlorine in 30 seconds and 7 ppm in 10 minutes.

#### EXAMPLE XI

A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|  |                                 |                 |  |     |
|--|---------------------------------|-----------------|--|-----|
|  | Ingredients                     | Parts by weight | Tabletting as described in Example I at 7000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 1 ppm of available chlorine in 30 seconds and 24 ppm in 10 minutes. One tablet added to 5 ml. of water containing 0.12 g. of citric acid (pH=2.2) delivered to the air space 4 ppm of available chlorine in 30 seconds and 38 ppm in 10 minutes. | 110 |
|  | Base formula                    | 62.1            |  |     |
|  | Trichloromelamine               | 14.0            |  |     |
|  | N—P <sub>2</sub> O <sub>5</sub> | 23.9            |  |     |
|  | Total                           | 100.0           |  | 110 |

#### EXAMPLE XII

A composition of the invention was prepared by blending thoroughly the following ingredients in the proportions indicated:

|  |                                 |                 |   |    |
|--|---------------------------------|-----------------|---|----|
|  | Ingredients                     | Parts by weight | Tabletting as described in Example I at 10,000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 4 ppm of available chlorine in 30 seconds and 11 ppm in 10 minutes. | 75 |
|  | Base formula                    | 7.0             |   |    |
|  | Chloramine T                    | 2.5             |   |    |
|  | N—P <sub>2</sub> O <sub>5</sub> | 0.5             |   |    |
|  | Total                           | 10.0            |   | 70 |

#### EXAMPLE XIII

A composition of the invention was prepared by thoroughly blending the following ingredients in the proportions indicated:

|  |  |                 |  |     |
|--|--|-----------------|--|-----|
|  | Ingredient   | Parts by weight | Tabletting as described in Example I at 7000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 1 ppm of available chlorine in 30 seconds and 7 ppm in 10 minutes. | 100 |
|  | Potassium dichloroisocyanurate                     | 8.31            |  |     |
|  | NaHCO <sub>3</sub> , powder                        | 13.00           |  |     |
|  | Citric acid, powder                                | 8.15            |  |     |
|  | Citric acid, fine granular                         | 8.15            |  |     |
|  | Microcel E   | 1.50            |  |     |
|  | NaCl, microsize                                    | 4.10            |  |     |
|  | Polyethylene, powder                               | 28.69           |  |     |
|  | Cab-O-Sil  | 3.50            |  |     |
|  | Carboxymethyl hydroxyethyl cellulose 37M, -70 mesh | 4.50            |  |     |
|  | Drierite, -40 mesh                                 | 14.60           |  |     |
|  | Sodium stearate                                    | 4.50            |  |     |
|  | Lithium stearate                                   | 1.00            |  |     |
|  | Total  | 100.00          |  | 95  |

Tabletting as described in Example I at 7000 psi and tested as described in Example I, a single tablet floated and disintegrated rapidly, delivering to the air space 1 ppm of available chlorine in 30 seconds and 7 ppm in 10 minutes.

One tablet added to 5 ml. of water delivered to the air space 2 ppm of available chlorine in 30 seconds and 24 ppm in 10 minutes. One tablet added to 5 ml. of water containing 0.12 g. of citric acid (pH=2.2) delivered to the air space 4 ppm of available chlorine in 30 seconds and 38 ppm in 10 minutes.

#### EXAMPLES XIV—XIX

Repetition of the procedures of Example

I substituting one of the following available chlorine compounds for lithium hypochlorite produced similar results:

|    | Example No. | Available Chlorine Compound                  |
|----|-------------|--|
|    | XIV         | 1,3 - Dichloro - 5,5 - dimethylhydantoin     |
| 5  | XV          | N,N' - Dichlorobenzoylene urea               |
|    | XVI         | Dichloramine T                               |
|    | XVII        | Magnesium hypochlorite                       |
|    | XVIII       | Barium hypochlorite                          |
| 10 | XIX         | Chlorinated trisodium phosphate (3.2% NaOCl) |

Our patent application No. 27612/66 (Serial No. 1,126,108) describes and claims a deodorizing tablet reactive with water to generate and deliver a chlorinous deodorizing gas into the air space above a body of water into which said tablet is introduced and on which said tablet floats, said tablet consisting essentially of a homogeneous mixture of the following ingredients:

- (1) calcium hypochlorite, 1 to 10 percent by weight;
- (b) alkali metal carbonate or bicarbonate, 5 to 25 percent by weight;
- (3) solid acid or acid salt, 5 to 25 percent by weight; and
- (4) polyolefin, 10 to 50 per cent by weight.

It also claims a method of deodorizing the air space above a body of water which consists in introducing such a tablet into said body of water. We make to claim herein to such a tablet or method and subject to this disclaimer,

#### WHAT WE CLAIM IS:—

1. A solid deodorizing composition reactive with water to generate and deliver a halogenous deodorizing gas into the air space above a body of water into which said composition is introduced and on which said composition floats, said composition comprising an intimate mixture of the following ingredients in particulate form:

- (1) a solid source of available chlorine or of available bromine;
- (2) a solid gas-generating source non-reactive with the solid source of available chlorine or bromine but reactive with water to generate a gas; and
- (3) a solid polymer of an aliphatic olefin having 2 to 5 carbon atoms.

2. A composition as claimed in claim 1 in which the solid source of available chlorine or bromine is a sodium dichloroisocyanurate.

3. A composition as claimed in claim 1 in which said solid source of available chlor-

ine or bromine is [(mono-trichloro)tetra-(monopotassium dichloro)]penta - isocyanurate.

4. A composition as claimed in any preceding claim in which said solid polymer is polyethylene or polypropylene.

5. A composition as claimed in any preceding claim in which said gas-generating source comprises an alkaline metal or alkaline earth metal carbonate or bicarbonate and a solid acid or acid salt.

6. A composition as claimed in claim 5 in which said carbonate is sodium carbonate.

7. A composition as claimed in claim 5 or 6 in which said acid is an organic acid.

8. A composition as claimed in claim 7 in which said organic acid is citric acid.

9. A composition as claimed in any preceding claim in which the proportions of said ingredients by weight are:

- (1) from 1 to 40 per cent;
- (2) from 5 to 50 per cent; and
- (3) from 10 to 50 per cent;

total, 100 per cent.

10. A composition as claimed in any preceding claim in which said composition is in tablet form.

11. A composition as claimed in claim 10 in which all the particles of said ingredients, prior to pressing into tablets, pass 30 mesh and at least 10 percent by weight of said particles pass 100 mesh.

12. A composition as claimed in claim 1, substantially as hereinbefore described in any of the Examples.

13. Method of deodorizing the air space above a body of water which consists in introducing into said body of water a composition as claimed in any preceding claim.

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